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MICROSTRUCTURAL MODELLING OF SELF-DESICCATION DURING HYDRATION

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ABSTRACT

A three-dimensional cellular automaton-based microstructural model has been applied to simulate the process of self-desiccation during the hydration of cement paste. As hydration occurs, the proper amount of empty pore space, corresponding to the chemical shrinkage of the cement paste, is created within the microstructure. This empty pore space in turn influences the future kinetics of the hydration process, as less water-filled space is available for the dissolution and precipitation of cement phases. Model predictions are compared with experimental data, including both SEM images of microstructure and measurements of degree of hydration based on non-evaporable water content. For water-to-cement ratios below 0.40, sealed curing conditions are seen to result in a significant decrease in the achievable hydration, relative to curing under saturated conditions. The addition of silica fume is observed to further increase the self-desiccation and decrease the achievable degree of hydration. The model can also be adapted to other curing scenarios, such as saturated curing until the capillary porosity becomes disconnected, followed by sealed curing, to assess the effects of different curing regimens on the hydration and subsequent performance of cement-based materials.

INTRODUCTION

As a concrete matures under sealed conditions, empty capillary porosity is created within its cement paste component due to the chemical shrinkage that accompanies the cement hydration reactions. This process was quantified many years ago by Powers¹⁾, but is also the subject of much recent research²⁻⁶⁾. The creation of empty capillary pore space has two major effects on the evolving cement paste system. First, the chemical shrinkage results in a reduction in the system's internal relative humidity (RH). Quantified by Gause and Tucker in 1940⁷⁾, this RH reduction can be quite substantial, with RH values as low as 70% measured for low (< 0.3) water-to-cement (w/c) ratio cement paste and concrete systems^{8,9)}. Based on the Kelvin-Laplace equation, this reduced RH will induce capillary pressures, $\sigma_{\text{capillary}}$, in the pore water described by:

$$\sigma_{\text{capillary}} = K\gamma = -\frac{\ln\left(\frac{\text{RH}}{100}\right)RT}{V_m} \quad (1)$$

where RH is the relative humidity expressed as a percentage, K is the average curvature of the surface of the condensed water, γ is its surface tension, R is the universal gas constant (8.314 J/(mol·K)), T is absolute temperature, and V_m is the molar volume of water. In turn, these capillary pressures will result in a measurable autogeneous shrinkage of the paste or concrete^{3,5,6}. According to equation (1), the induced capillary pressures will be seven times greater in a system with an RH of 70% compared with one with an RH of 95%, which may be one reason why low w/c ratio concretes are often more susceptible to early age cracking.

The second effect of the creation of empty capillary pores is a change in the hydration kinetics of the cement paste^{10,11}. Because cement hydration reactions generally proceed by a dissolution/precipitation mechanism and the empty pore space created due to self-desiccation is no longer available to be filled with hydration products, the hydration will slow down and effectively terminate at a lower degree of hydration than could be achieved under saturated conditions. The remainder of this paper will focus on this latter effect, using a combination of experimental and computer modelling techniques to quantify the effects of curing conditions on the measured degree of hydration of a variety of cement pastes with and without silica fume additions.

EXPERIMENTAL PROCEDURES

Saturated and Sealed Specimens

Composition and properties of the two ASTM Type I portland cements used in this study, Cements 115 and 116 issued in 1995 by the Cement and Concrete Reference Laboratory at NIST, can be found elsewhere^{12,13}. The cement and the necessary mixing water, $w/c=0.30$, were conditioned at 25 °C overnight and then mixed together by hand in a sealed plastic bag for two to three minutes. Paste samples on the order of ten grams were stored in capped plastic vials at 25 °C until measuring the non-evaporable water content, typically after ages of 1, 3, 7, 14, 28, 56, and 90 days. For the saturated samples, approximately 1 mL of water was added on top of the cement paste to provide water throughout the experiment. Non-evaporable water was quantified as the mass loss between 105 °C and 950 °C, corrected for the loss on ignition of the dry cement powder, assessed in a separate measurement. These values were converted to degrees of hydration based on similar measurements performed on fully hydrated specimens ($w/c=3.0$, continuously rotated in a jar mill for 28 days), which yielded values of 0.226 and 0.235 g H_2O/g cement for Cements 115 and 116, respectively. 28 days in a jar mill was deemed sufficient to achieve complete hydration, as no further hydration was observed when the curing was extended to 42 days. For Cement 115, two samples, one saturated and one sealed, were removed after 94 days of curing and prepared for viewing in the scanning electron microscope (SEM).

Computer Simulations

In addition to the experimental studies, computer simulations were performed using the NIST cement paste microstructural model^{12,13}. This model employs a sequence of dissolution/diffusion/reaction cycles to simulate the hydration reactions between cement particles and water. Typically, the cement paste microstructure is represented within the computer as a cubic volume 100 pixels on a side, with each pixel corresponding to a volume of 1 μm^3 . Hydration is simulated using a cellular automata approach to repetitively update the phases/species present at each pixel in the microstructure¹³.

In this study, for each of the two cements, initial 3-D cement particle images, based on their measured particle size distributions and the phase area and perimeter (surface) fractions measured on 2-D SEM/X-ray images¹²⁾, were created for $w/c=0.30$ and $w/c=0.40$. These 3-D systems were then "computationally hydrated" under saturated and sealed conditions. For saturated conditions, it is assumed that all capillary porosity remains water-filled throughout the hydration process. In the case of sealed (self-desiccating) conditions, the computer model creates empty pore space as the hydration occurs to account directly for the chemical shrinkage¹³⁾, which is typically on the order of 0.06 mL H_2O/g cement hydrated. This empty pore volume is computed as the difference between the total capillary porosity and the volume of water not yet incorporated into hydration products after each cycle of the simulated hydration. In an attempt to model the actual physical process, the largest pores are emptied first, and no hydration products are deposited in pores which have been emptied. A previous calibration of model cycles to real time^{12,13)} for hydration under saturated conditions was then applied to create model degree of hydration vs. time curves for both saturated and sealed curing conditions to compare with the experimental counterparts. In addition, two-dimensional slices from the "fully hydrated" (i.e., 5000 cycles of hydration) three-dimensional computer model microstructures were created to compare to the SEM images for the saturated and sealed curing conditions for Cement 115 with $w/c=0.30$.

Recently, to predict the adiabatic response of a wide variety of concretes, the NIST microstructural model has been modified to include the pozzolanic reaction between silica fume and calcium hydroxide¹⁴⁾, forming a pozzolanic *C-S-H* with a stoichiometry of $C_{1.1}SH_{3.9}$ and a molar volume of 101.81 $cm^3/mole$. The stoichiometry and molar volume were chosen to be consistent with phase composition and chemical shrinkage results presented in the literature^{6,15-17)}. The reaction corresponds to an additional chemical shrinkage of 0.20 mL H_2O/g silica fume reacted. Thus, systems containing silica fume, if they hydrate to the same degree, will undergo a greater amount of chemical shrinkage than those without silica fume. The effects of silica fume replacement on hydration kinetics during sealed curing were investigated using the microstructural model for Cement 116 with 5% and 10% replacement levels of silica fume, while maintaining a constant water to solids (cement plus silica fume) ratio (w/s) of 0.40.

RESULTS

FIG.-1 compares the degree of hydration achieved under saturated and sealed conditions for the two cements studied, for $w/c=0.30$. For both cements, the sealed conditions are observed to reduce the achieved hydration, particularly at times exceeding 7 days. At early times, the newly created empty capillary porosity has only a minor effect on the hydration kinetics as a significant volume fraction of water-filled capillary pore space still exists. For $w/c=0.30$, initially, about 50% of the cement paste volume is filled with water. However, as water is consumed by the hydration reactions, the fraction of empty pore space relative to that which is water-filled becomes significant, and a substantial reduction in the hydration rate is observed. The predicted results based on the NIST cement paste microstructural model are seen to closely follow the experimental values, particularly for Cement 115.

Simulations performed for the two cements with $w/c=0.40$ have indicated smaller differences in the hydration kinetics between curing under saturated and sealed conditions. For Cement 115, the "final" achieved degrees of hydration after 5000 cycles of the hydration model were 0.88 and 0.83 for the saturated and sealed conditions, respectively. The

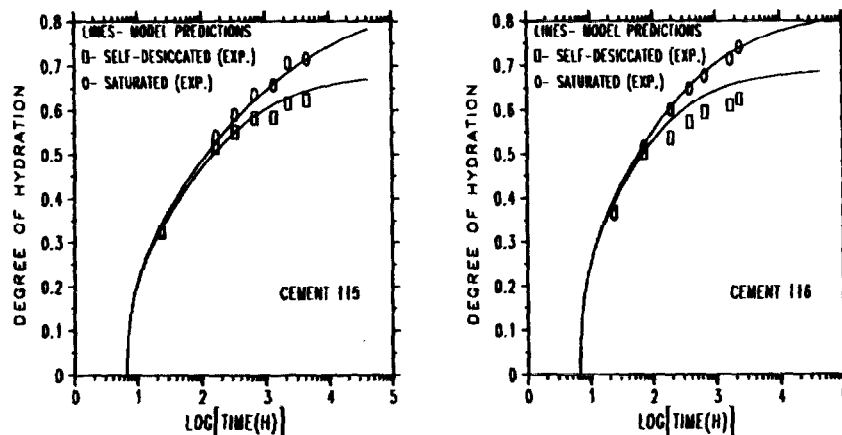


FIG.-1: Comparison of saturated and sealed (self-desiccated) hydration for Cements 115 and 116 with $w/c=0.30$.

corresponding values for Cement 116 were 0.90 and 0.85. These differences of 0.05 can be compared with the difference of about 0.10 for the $w/c=0.30$ systems as shown in FIG.-1. In addition, the differences to be expected after 28 days of curing, for example, were less than those for the $w/c=0.30$ systems (on the order of 0.01 for Cement 115 and 0.03 for Cement 116). Furthermore, experimental determinations have indicated basically no difference in the degrees of hydration achieved after 28 days curing for $w/c=0.5$ cement pastes cured under saturated and sealed conditions, in agreement with simulation results. Thus, as expected, the effects of self-desiccation on hydration kinetics are seen to definitely become more prominent at lower (< 0.4) w/c ratios.

The model can be further validated against experiment by comparing SEM micrographs of real sample microstructures to two-dimensional images from the 3-D model. Figures 2 and 3 provide such a comparison at similar scales for Cement 115 with $w/c=0.30$. The two most distinguishing features between the sealed and saturated specimens are the area and size of the unhydrated cement grains and the area and size of the observable capillary pores. One can clearly observe that there are more and larger unhydrated cement grains in the sealed specimens (particularly in terms of the alite grains which are surrounded by a dense layer of calcium silicate hydrate gel), in agreement with their measured lower degrees of hydration. Based on quantitative SEM measurements of the unhydrated cement area fractions, after 94 days, the saturated sample has achieved a degree of hydration of 0.79 ± 0.03 while the sealed sample has only achieved a value of 0.66 ± 0.04 , based on the averages from eleven fields of view ($1024 \text{ pixels} \times 800 \text{ pixels}$, $0.25 \mu\text{m/pixel}$) for each sample, and expressed with an uncertainty of one standard deviation. The corresponding degrees of hydration for the two model systems shown are 0.80 and 0.69, respectively. In addition, due to the emptying of the capillary pores due to chemical shrinkage, many relatively large pores remain in the sealed specimens. Once again, the effects observed in the real specimens are duplicated reasonably well by the model, as the real and model images appear quite similar.

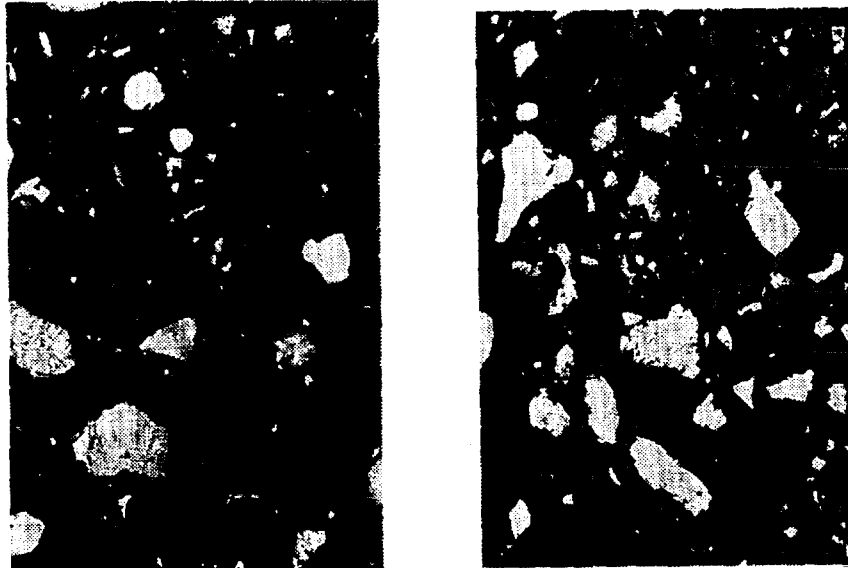


FIG.-2: Comparison of real SEM images for saturated (left) and sealed (right) hydration for Cement 115 with $w/c=0.30$ after 94 days of curing. Unhydrated cement is white, porosity is black, calcium hydroxide is light grey, and calcium silicate hydrate gel and other hydration products are dark grey. Areas imaged are approximately $128\ \mu\text{m} \times 190\ \mu\text{m}$.

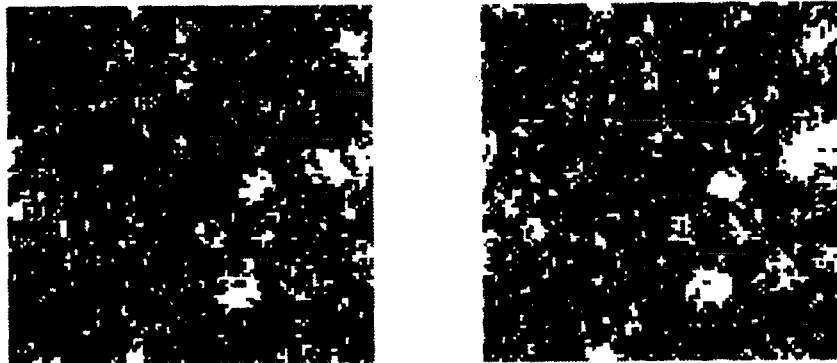


FIG.-3: Comparison of model images for saturated (left) and sealed (right) hydration for Cement 115 with $w/c=0.30$. Greyscale assignments are the same as those given above for the real images. Areas represented by the images are $100\ \mu\text{m} \times 100\ \mu\text{m}$.

The model can also be used to explore the effects of different curing regimens on achievable hydration. For example, many years ago, Powers¹⁰⁾ suggested maintaining saturated curing conditions only until the capillary porosity depercolates, as beyond this point, it may be difficult to maintain internal saturation. Analysis of microstructures generated using a monophase cement microstructural model¹⁸⁾ have indicated that this depercolation occurs at a capillary porosity of about 20%, for w/c ratios below 0.6, in general agreement with the earlier experimental results of Powers¹⁹⁾. To explore the effect of this curing regimen on hydration, simulations were conducted for Cement 116 with w/c=0.30 in which empty capillary porosity due to chemical shrinkage was only created after the system capillary porosity had fallen below 20%, which occurs at a degree of hydration of about 0.5. FIG.-4 shows the resultant degree of hydration vs. cycles curve, in comparison with the equivalent curves for hydration under saturated and sealed curing conditions. For these simulations, 5000 cycles of hydration would correspond to approximately 4 years of curing at 25 °C. The "sealed after 20% porosity" curve is seen to most closely follow the completely saturated curve, supporting the criticality of proper early curing practices for achieving a durable concrete.

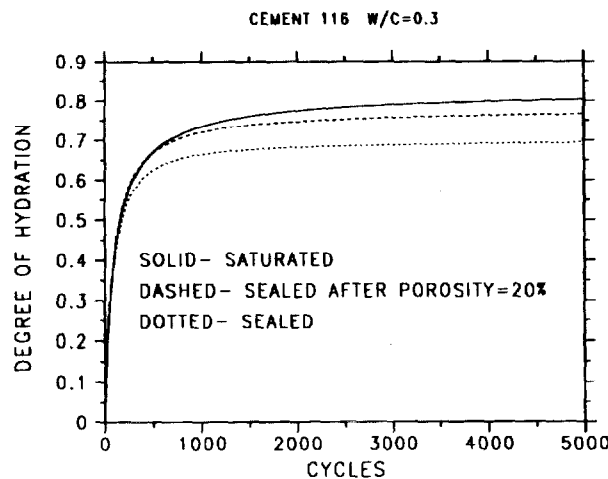


FIG.-4: Comparison of hydration under different curing regimens.

Simulations have also been performed to assess the effects of silica fume additions on the self-desiccation and achievable hydration. FIG.-5 shows the effects of 5% and 10% silica fume replacements (maintaining a constant water-to-solids, w/s, mass ratio of 0.40) on the simulated degree of hydration vs. cycles curves. The addition of silica fume has minimal effects on the early hydration kinetics but results in significantly less hydration being achieved at later ages, for curing under sealed conditions. For a w/c ratio below about 0.42, there is already insufficient water to achieve complete hydration of the cement, so that the consumption of additional water due to the pozzolanic reaction only intensifies this effect and further limits the achievable hydration.

The porosities of the cement pastes before and after hydration are summarized in TABLE-1. Because of the lower specific gravity of silica fume and the fact that the re-

placements are made on a mass basis, there is a slightly lower initial capillary porosity in the systems containing silica fume. The final total porosities of the three systems are comparable, but the water-filled porosities are reduced in the systems containing silica fume due to its increased water demand. Even though the early time hydration kinetics are similar for the three systems, there is more empty porosity in the systems containing silica fume, as the chemical shrinkage per unit mass of cement reacted is significantly increased by the pozzolanic reaction, as indicated in Table 1. In addition, as pointed out by Jensen and Hansen⁶⁾, for a given volume of chemical shrinkage, the smaller pore sizes emptied in the systems containing silica fume will result in a greater RH reduction. This will in turn lead to greater self-desiccation stresses as indicated by equation (1), perhaps making concretes containing silica fume particularly susceptible to early age cracking.

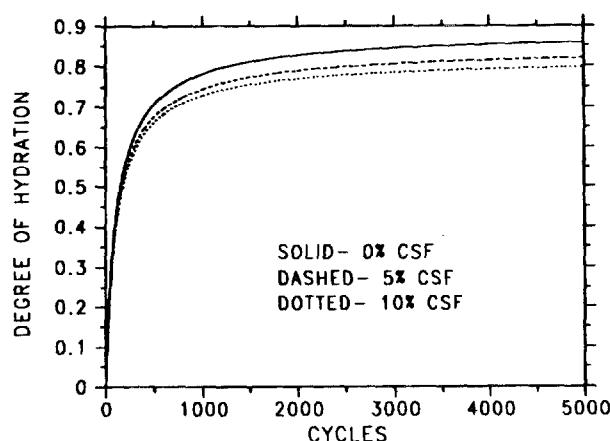


FIG.-5: Effect of silica fume (CSF) replacement on hydration under sealed conditions, Cement 116 with $w/c=0.40$.

TABLE-1: Capillary Porosities for Simulated Cement Pastes ($w/s=0.40$)

Silica Fume Replacement (%)	Initial Porosity (%)	Final Water-Filled Porosity (%)	Final Total Porosity (%)	Chemical Shrinkage per mass of cement hydrated (mL/g)
0	56.2	5.6	13.7	0.068
5	55.6	4.7	13.4	0.081
10	55.0	4.4	13.4	0.092

CONCLUSIONS

The NIST microstructural model has been applied to examine the effects of self-desiccation on the hydration kinetics of low w/c ratio cement pastes. The model successfully predicts

the observed reduction in achievable hydration at longer curing times, as the empty capillary pores eventually influence the progress of the hydration reactions. The effects of self-desiccation on hydration kinetics are more significant the lower the w/c ratio, with larger differences predicted for the w/c=0.30 than for the w/c=0.40 cement pastes. The model also indicates that the curing regimen of maintaining saturation until the capillary porosity depercolates, first suggested by Powers¹⁰⁾, results in long term degrees of hydration which approach those achievable under totally saturated conditions. Thus, the early time curing procedure may have a critical influence on ultimate performance. Simulations with silica fume replacements of 5% and 10% indicate that the pozzolanic reaction increases the chemical shrinkage and thus further decreases the achievable degree of hydration. This increased chemical shrinkage, coupled with the smaller pore sizes present in systems containing silica fume, may render low w/c ratio concretes containing silica fume especially susceptible to self-desiccation and subsequent early age cracking, due to the enhanced RH reduction at early ages.

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